

# Rheological Evaluation of Surfactants with Potential Application as Divergent Agents

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**Abstract**-Viscoelastic surfactants are very useful in various oilfield operations, such as enhancing oil recovery and hydraulic fracturing and acidification. Because of the permeability differences in the rock reservoir, a large part of the fluid injected can migrate to undesired regions. Therefore, viscous fluids are used to modify the permeability of certain regions of the rock formation. The products added to the fluids that provide this characteristic are called divergent agents. There are a large number of commercial products that can be used for this purpose, but the fluids prepared with them must have special properties. Therefore, it is essential to evaluate these products in advance. This work examines the chemical structure and physic-chemical properties of commercial surfactants to identify those with potential application as divergent agents. To do this, the rheological behaviour of the commercial formulations was tested considering temperature and pH conditions typical of reservoirs.

**Keywords**-Divergent Agents; Surfactants; Rheology; Surface Tension; FTIR

## I. INTRODUCTION

Extraction of petroleum requires the use of various processes. Many of these involve injection of fluids in the porous formations where the oil is found, for example acidification, hydraulic fracturing and scale inhibition.

Hydrocarbon reservoirs are constituted of layers with different permeabilities, due to natural phenomena or invasion of mud. Therefore, when a fluid is injected into the rock formation, it will preferentially migrate to the more permeable zones around the bore hole, leaving the zones that mostly need of treatment intact. It is thus necessary to use a technique that induces the process fluid to diverge to zones with low permeability, allowing a more uniform fluid distribution among the various zones. This is achieved by temporarily obstructing the more permeable zones by using a fluid containing additives called divergent agents, to permit treatment of less permeable zones [1-11].

In the majority of applications of this technique, an initially low-viscosity polymer solution is injected in the reservoir. Upon reaching the target zone, the solution becomes more viscous, reducing the permeability of that part of the reservoir. This can be achieved by the transformation of the solution into a gel, either spontaneously or by chemical induction [7].

These solutions often present non-Newtonian behaviour, i.e., their viscosity depends on the flow rate (more specifically, the shear rate). The most common behaviour presented by these polymer solutions is pseudo-plastic, in which the viscosity declines with an increase in the shear rate. In certain cases the solution has low viscosity when flowing through pipes and during injection toward the rock formation's pores.

Then the solution migrates radially through the formation, the flow rate and associated shear rate decline and the solution's viscosity increases. In many oilfield operations, this increased viscosity with reduced flow rate creates a gel that is sufficiently strong to have the desired divergent effect [11].

Many reticulation agents have been used. They can be classified as the inorganic (for example, chrome, zirconium, aluminium and borate) or the organic (phenol/formaldehyde, aldehydes or acetates, polyamides) [7,12,13].

The reservoir conditions are relatively aggressive to certain injected substances due to variations in temperature, salinity, pH and other observable factors.

Currently there are few gels that can be used under adverse conditions. The polymers used in these gels include polyacrylamides with low molar mass, natural polymers and special polymers developed to tolerate these conditions. Metallic reticulation agents can be used to produce gels with anionic polymers. This is achieved through the formation of ionic bonds between multivalent captions and negative sites of the polymer. The gels produced through metallic reticulation agents typically are less thermally stable. Organic reticulation involves the formation of covalent bonds between functional groups of the polymer and the reticulation agent, connecting two or more polymer chains. To obtain thermally stable gels, it is necessary to start with thermally stable polymers [7].

The use of viscoelastic surfactants in aqueous fluid systems has also been reported. The surfactants being used are mixed ionic or amphoteric, such as dihydroxyl alkyl glycinate, alkyl betaine, alkyl amidopropyl betaine and e alkylamino mono- or di- propionate, derived from certain waxes, fats and oils. The surfactant is used together with inorganic salts, organic acids and organic acid salts or combinations of these additives [14].

This paper reports the results of studies of the rheological behavior of aqueous formulations of a series of surfactants, in comparison with two commercial divergent agent formulations.

## II. EXPERIMENTAL

### A. Surfactant Systems

The surfactant systems used in this work were donated by Rhodia do Brasil, SP-Brazil described below.

- System S1
  - Mixture of butyl ether hydroxypropyl sultaine and 2-ethyl-hexyl ether hydroxypropyl sultaine – 50% and 43%
  - NaCl – 7.16%

- Water
- System S2
- Cocamidopropyl hydroxyl sultaine – 49.57%
- Color gardner – 0.2%
- NaCl – 6.65%
- Water
- System S3
- Dihydroxyethyl tallow glycinate (betaine) – 41.8%
- NaCl – 5.3%
- Water
- System S4
- Sodium lauriminodipropionate (28 to 31%)
- Water (69 a 72%)
- pH: 6-7
- System S5
- Sodium alkyliminopropionate (41 to 44%)
- Methanol (6-8%)
- Water (48 to 51%)
- pH: 10-11
- System S6
- Ethoxylated alkyl sodium sulphate (25-28%)
- Water (72-75%)
- Dioxane (<0.09%)
- Ethylene oxide (<0.001%)
- System S7
- Sodium alkyl ether sulphate (69-71%)
- Water (29-31%)
- Dioxane (<0.009%)
- Ethylene oxide (<0.001%)

The commercial divergent agent formulations utilized (system C1 and system C2), as well as the procedure of preparing each of the fluids, are reported below.

#### • System C1

System C1 is supplied ready to use by the manufacturer. We only added ammonium chloride salt ( $\text{NH}_4\text{Cl}$ ) to increase its viscosity. The base composition is the following:

- Aliphatic amine derivative (base surfactant) – 60-100%;
- 2-propanol – 10-30% p/v;
- 1,2-propanediol – 10-30% p/v;
- Water – 5-10% v/v.

Before adding the salt to system C1, we pipette two 5-mL aliquots into aluminium capsules, previously weighed, to calculate the concentration of the base surfactant in the formulation. The aliquots were placed in a circulating air

chamber at 100 °C and left there until the aluminium capsules reached constant weight. The base surfactant concentration determined by this method was 61% wt/v.

To add the salt to the system, we first dissolved  $\text{NH}_4\text{Cl}$  in water at a concentration of 4% wt/v. The final formulation was prepared by slowly adding 25 mL of the base formulation to the brine, under mechanical stirring at 1000 rpm. After the addition was completed, the stirring speed was increased to 2000 rpm for about 30 minutes.

#### • System C2

System C2 is composed of an amphoteric surfactant (base surfactant), to which other components are added according to the manufacturer's orientation.

The ammonium chloride was added in distilled deionised water and stirred with a glass rod until completely dissolved. Then KOH was added until it was completely dissolved as well as the base surfactant. This mixture was homogenized using a mechanical stirrer at 2000 rpm for 20 minutes. Finally, the BF-7 LB compound was added until a gel formed, and this mixture was stirred for an additional 30 minutes at 2000 rpm. The final composition of system C2 was as follows:

- Industrial water – 4% v/v;
- Ammonium chloride – 4% wt/v;
- KOH – 0.5% wt/v;
- Amphoteric surfactant (base surfactant) – 3% wt/v;
- BF-7LB – 0.8% v/v

### B. Chemical Characterization of the Base Surfactants

The structure of the base surfactants was characterized by qualitative analyses in a Perkin Elmer 1720x Fourier transform infrared (FT-IR) spectrometer, controlled by a DEC 320 sx station computer, with an IR data manager, also made by Perkin Elmer. We used the capillary film method, in which the samples are spread over a KBr cell and the film formed is covered with another KBr cell. All the analyses were performed using resolution of 2  $\text{cm}^{-1}$ , 20 scans and a wavelength range of 4000-400  $\text{cm}^{-1}$ .

The systems C1 and C2 were also analysed by nuclear magnetic resonance (NMR) in a Varian Mercury 300 spectrometer, at the following experimental settings: observed nucleus -  $^1\text{H}$ ; frequency - 300.067 MHz; concentration - ~ 1% wt/v; internal reference – tetramethylsilane (TMS).

Finally, we evaporated the samples in a vacuum chamber to eliminate solvents and other possibly volatile constituents. This treatment does not eliminate the salts present in the samples.

### C. Analysis of the Surface Tension of the Surfactant Systems

We measured the surface tension of the solutions in triplicate, at 25°C, in a Krüss K10ST digital tensiometer. For each sample, we plotted a graph of the average surface tension (in  $\text{mNm}^{-1}$ ) against the logarithm of the concentration (in %wt/v). We then used this graph to determine the critical micelle concentration (CMC).

### D. Rheological Evaluation of the Surfactant Systems

We performed the rheological evaluation in a Haake RS600 rheometer.

Depending on the viscosity value, it used coaxial cylinders (Z20 and DG41) or a cone/plate accessory, with cone diameters of 35 and 60 mm and an angle of 1°. We analysed the systems at temperatures of 25 and 5 °C and pH interval of 1 to 14. We carried out these analyses in function of the increase and decrease of the shear rate. Since the systems are intended for an application where the fluid will be submitted to a certain shear rate and then a lower one, we recorded the viscosity values as the shear rate was being reduced.

### III. RESULTS AND DISCUSSION

#### A. Chemical characterization of the Base Surfactants

The probable structures of the base surfactants of the various systems, given by the manufacturers and confirmed by the spectrometric analyses, are listed in Table I. By the chemical structures of surfactants and data of surface tensions and CMC, we expected to establish some kind of relationship with the rheological performance of the systems.

TABLE I PROBABLE STRUCTURES OF THE SYSTEMS BASE

System	Classification of the manufacturer	Probable structures of the base surfactants
S1	Mixed ionic surfactant: mixture of butyl ether hydroxypropyl sultaine and 2-ethyl-hexyl ether hydroxypropyl sultaine	$\begin{array}{c} \text{OH} \quad \text{CH}_3 \\   \quad   \\ \text{R-O-CH}_2\text{CHCH}_2\text{-N}^+\text{-CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^- \\   \\ \text{CH}_3 \end{array}$
S2	Mixed ionic surfactant: Cocamidopropyl hydroxyl sultaine	$\begin{array}{c} \text{O} \quad \text{CH}_3 \quad \text{OH} \\    \quad   \quad   \\ \text{R-C-NH-CH}_2\text{CH}_2\text{CH}_2\text{-N}^+\text{-CH}_2\text{CHCH}_2\text{SO}_3^- \\   \\ \text{CH}_3 \end{array}$
S3	Mixed ionic surfactant: Dihydroxyethyl tallow glycinate (betaine)	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\   \\ \text{R-N}^+\text{-CH}_2\text{COO}^- \\   \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$
S4	Amphoteric surfactant: Sodium laurimino dipropionate	$\begin{array}{c} (\text{Na}^+ \text{ } ^-\text{OOC-H}_2\text{C-H}_2\text{C})_2\text{C=N}^+\text{H} \\   \\ \text{CH}_2\text{-(CH}_2\text{)}_{10}\text{-CH}_3 \end{array}$
S5	Amphoteric surfactant: Sodium alkylimino propionate	$\begin{array}{c} \text{Na}^+ \text{ } ^-\text{OOC-H}_2\text{C-H}_2\text{C-HC=N}^+\text{H} \\   \\ \text{R} \end{array}$
S6	Ethoxylated alkyl sodium sulphate	$\text{R}_1\text{-(O-CH}_2\text{-CH}_2\text{)}_n\text{-OSO}_3^- \text{Na}^+$
S7	Sodium alkyl ether sulphate	$\text{R}_1\text{-(O-CH}_2\text{-CH}_2\text{)}_n\text{-OSO}_3^- \text{Na}^+$
C1	Amphoteric surfactant	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\   \\ \text{R-N}^+\text{H} \\   \\ \text{CH}_2\text{CH}_2\text{COO}^- \end{array}$
C2	Amphoteric surfactant	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{COOMe} \\   \\ \text{R-N}^+\text{H} \\   \\ \text{CH}_2\text{CH}_2\text{COO}^- \text{Na} \end{array}$

#### B. Measurement of the Surface Tension and Critical Micelle Concentration of the Surfactants

Table II presents the surface tension values of the aqueous solutions containing each base surfactant, at concentrations of 10-4 and 0.3% v/v, and the CMC values. Systems S1 and S7

were not analysed because these formulations presented phase separation when diluted in water.

TABLE II  
SURFACE TENSION AND CMC RESULTS OF THE SYSTEMS

System	Initial surface tension (mNm <sup>-1</sup> ) <sup>(a)</sup>	Final surface tension (mNm <sup>-1</sup> ) <sup>(b)</sup>	CMC (% v/v)
S1	-	-	-
S2	70	32	10 <sup>-2</sup>
S3	65	36	10 <sup>-2</sup>
S4	69	33	10 <sup>-2</sup>
S5	71	39	3 x 10 <sup>-1</sup>
S6	65	33	8 x 10 <sup>-2</sup>
S7	-	-	-
C1	56	35	2x10 <sup>-3</sup>
C2	69	30	10 <sup>-2</sup>

(a) Initial surface tension obtained at a concentration of 10<sup>-4</sup> % v/v

(b) Final surface tension obtained at a concentration of 0.3 % v/v

Except for system C1, all the others behaved similarly at a base surfactant concentration of 10-4 % v/v, that is, the surface tensions of the solutions were at ~70 mNm<sup>-1</sup>. At concentrations above the CMC these values declined to around 35 mNm<sup>-1</sup>, and the CMC values were above 10-2 % v/v. On the other hand, system C1, at a low base surfactant concentration (10-4 % v/v), already reduced the surface tension of the water to nearly 56 mNm<sup>-1</sup>, and also had the lowest CMC (2 x 10<sup>-3</sup> % v/v). Only the surface tension values at concentrations above the CMC were similar to those found for the other solutions of the products tested.

Because system C1 presented the lowest surface tension at low concentration and the smallest CMC *Except for system C1*, all the others behaved similarly at a base surfactant concentration of 10-4 % v/v, that is, the surface tensions of the solutions were at ~70 mNm<sup>-1</sup>. At concentrations above the CMC these values declined to around 35 mNm<sup>-1</sup>, and the CMC values were above 10-2 % v/v. On the other hand, system C1, at a low base surfactant concentration (10-4 % v/v), already reduced the surface tension of the water to nearly 56 mNm<sup>-1</sup>, and also had the lowest CMC (2 x 10<sup>-3</sup> % v/v). Only the surface tension values at concentrations above the CMC were similar to those found for the other solutions of the products tested. Besides performing the best in the rheological analyses (see latter), we performed analyses of the surface tension versus concentration, varying the pH of this system through the addition of hydrochloric acid or sodium hydroxide. The results are shown in Table III.

TABLE III SURFACE TENSION AND CMC RESULTS OF SYSTEMS C1 WITH DIFFERENT PH VALUES

pH	Initial surface tension (mNm <sup>-1</sup> ) <sup>(a)</sup>	Final surface tension (mNm <sup>-1</sup> ) <sup>(b)</sup>	CMC (% v/v)
2	70	34	3 x 10 <sup>-3</sup>
6	56	35	2 x 10 <sup>-3</sup>
13	55	34	1.5 x 10 <sup>-3</sup>

(a) Initial surface tension obtained at a concentration of 10<sup>-4</sup> % v/v

(b) Final surface tension obtained at a concentration of 0.3 % v/v

At a surfactant concentration of 0.3%, the surface tension values were similar in all three pH conditions tested. This result is coherent with the fact that the same structure occupies the interface in all three cases, and above the CMC the interface is totally (or nearly all) occupied by the surfactant species, that is, under the three conditions the structure is the same, with the same concentration at the interface, so the surface tension values are equal. However, at a concentration of 0.0001 % the surface tensions were quite different for pH 2. This behaviour is related to the fact that the amphoteric surfactant assumes a cationic form at low pH. In the specific case of the surfactant studied, the  $N^+$  group, which interacts more strongly with water than the  $-COO^-$  and  $-O^-$  groups do [15], makes the surfactant more hydrophilic, and at a given concentration, fewer species migrate to the interface, resulting in higher surface tension, that is, a lower value but near that of pure water. This behavior could also be observed with respect to the CMC values, because the cationic species, which is more soluble in water, has a higher CMC than the zwitterionic or anionic species do.

### C. Rheological Evaluation of the Surfactant Systems

#### 1) Tests in Function of the Shear Rate and Temperature:

According to the literature [7], formulations considered good for use as divergent fluids must possess, among other aspects, viscosity values between 10 and 20 cP at 50°C and shear rates around 70 s<sup>-1</sup>. Besides this, when the shear rate falls to 10 s<sup>-1</sup>, the formulation's viscosity cannot vary drastically (up to ~ 60 cP), and the desired behavior of the fluid should be moderately pseudo-plastic.

he tests of viscosity in function of shear rate were running at two temperatures to obtain two curves for each condition: tests with increasing and decreasing shear rates. In general, the curves obtained during the tests with rising shear rate coincided with those obtained during the falling shear rate tests. Figure 1 shows the curves obtained for system S5 as an example of the pseudo-plastic character and the differences observed as a function of the cycle measured (increasing or decreasing shear rate) for this system. Table 4 compiles all the results: viscosity values at two temperatures (25 and 50°C) and two shear rates (70 and 10 s<sup>-1</sup>). These values were taken from the curves of the viscosity in function of shear rate described during the falling rate tests. System S2 formed a thick film during the analysis at 50°C, and for this, its results are omitted from Table IV.

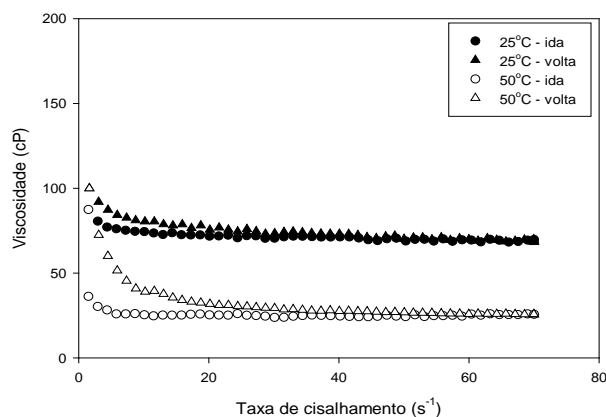


Fig. 1 Viscosity curves as a function of shear rate of system S5, at temperatures of 25 and 50°C

TABLE IV VISCOSITY RESULTS OF OBTAINED IN TESTS AT VARYING SHEAR RATES, AT 25, 50 AND 70 °C

System	Viscosity (cP)			
	25 °C		50 °C	
	70 s <sup>-1</sup>	10 s <sup>-1</sup>	70 s <sup>-1</sup>	10 s <sup>-1</sup>
S1	10	12	3	5
S2	90	90	**	**
S3*	50	114	5	9
S4	28	30	18	44
S5*	70	80	25	39
S6	24	25	26	200
S7	1,670	5,100	1,700	7,200
C1	70	335	65	130
C2	10	830	10	10

\*Sample diluted in water in a proportion of 1:10 due to the gel form, which hampered viscosity measurement.

\*\*The system was not measured at this temperature due to evaporation, evidenced by the formation of a film on the sample's surface.

The formulations of systems S3 and S5 supplied by the manufacturer showed high viscosity, with various bubbles trapped inside the gel formed. For this reason, we diluted these formulations in water in a proportion of 1:10 before performing the viscosity measurements.

As expected, the viscosity of all the systems fell with the increase in temperature, at both shear rates, with the exception of systems S6 and S7, which have an ethoxylated structure. This behavior is due to the reduction of their interactions with water as increasing temperature, until complete phase separation at a temperature above 50°C.

In general, the systems showed pseudo-plastic behavior at the two temperatures tested, and the viscosity values were higher at lower shear rates. Since the main temperature of interest for application of divergent fluids is 50°C, systems S2 and C2 could be eliminated because they do not have the required pseudo-plastic behavior at this temperature.

With respect to the ideal viscosity values at 50°C, system S1 was much less viscous than desired. In an attempt to raise these values, we added NH<sub>4</sub>Cl at a concentration of 4% wt/v to this system, but there was no change in viscosity.

Therefore, all the systems had the desired behaviour except for S1, S2 and C2, suggesting that the desired viscosities can be achieved just with adjustment of the concentration.

Because of the importance of knowledge of the behaviour of divergent fluid systems at the varied pH that can be found under oilfield conditions, we evaluated all the systems at different pH values, at a temperature of 25°C, even those that did not present the desired pseudo-plastic behaviour. We chose this temperature for the initial tests because it allows easier measurement. Table V shows the viscosity results at shear rates of 70 and 10 s<sup>-1</sup>.

TABLE V VISCOSITY RESULTS OBTAINED IN TESTS WITH VARYING SHEAR RATES AT 25 °C, UNDER DIFFERENT PH CONDITIONS

System	Viscosity at 25 °C (cP)						
	70 s <sup>-1</sup>						
	2	4	6	8	10	12	13
S1	-	10	10	**	**	11	-
S2	-	89	91	90	95	-	-
S3*	-	48	50	-	-	-	-
S4	-	-	27	33	-	-	-
S5*	-	3	**	**	70	-	-
S6	-	38	**	24	**	**	315
S7	-	-	-	-	-	-	-
C1	70	70	70	70	70	70	70
C2	-	-	-	10	-	-	-
	10 s <sup>-1</sup>						
	2	4	6	8	10	12	13
S1	2	4	6	8	10	12	13
S2	-	12	12	**	**	13	-
S3*	-	85	91	90	96	-	-
S4	-	110	114	-	-	-	-
S5*	-	-	47	35	-	-	-
S6	-	3	**	**	80	-	-
S7	-	34	**	25	**	**	411
C1	-	-	-	-	-	-	-
C2	332	332	335	330	328	326	325
S1	-	-	-	830	-	-	-

\* Sample diluted in water in a proportion of 1:10 due to the gel form, which hampered viscosity measurement.

\*\* Analyses not performed

(-) Viscosity values not determined due to limitations of the technique or inadequacy of the formulations.

The viscosity values in boldface refer to those of the original formulation without the addition of hydrochloric acid or potassium hydroxide

Among the formulations that maintained their viscosity values in the pH range tested were S1, S6, and C1. System S1 had already been eliminated because of its very low viscosity values. System S6 resisted the pH variations, but there were significant viscosity changes at extreme pH values. The other systems presented phase separation with the pH variation or their viscosity values fell outside the detection range of the device.

Therefore, systems S6 and C1 were indicated for further testing at 50°C, under the same pH conditions tested previously. However, we only tested system C1. That is because system S6, at 50 °C and pH 8 (Table 4) did not show the desired pseudoplastic behaviour (viscosities of 26 and 200 cP, respectively at 70 and 10 s<sup>-1</sup>).

System C1 maintained its resistance to pH even at a temperature of 50 °C, and showed viscosities of about 1,700 and 7,200 cP, respectively, for shear rates at 70 and 10 s<sup>-1</sup>.

We performed other rheological tests of system C1 to verify its stability over time. For this purpose we chose shear

rates at 10, 70, and 500 s<sup>-1</sup> for the tests in function of time (30 minutes). No significant thixotropic behaviour was observed, meaning this system maintained the viscosity shown in Table 4 even after applying shear for 30 minutes.

## 2) Viscoelasticity Tests

We only performed viscoelasticity tests on system C1 since it was the only one that presenting viscosity values in the desired range, as well as having good resistance to pH variation. The first tests were carried out at a frequency of 1Hz, with variation of the amplitude. Figure 2 shows a region of linear viscoelasticity, that is, the region where the material's viscoelastic structure remains intact (up to a stress of 1 Pa). Besides this, it can be seen that the elastic component is much greater than the viscous component, which is expected of a gel.

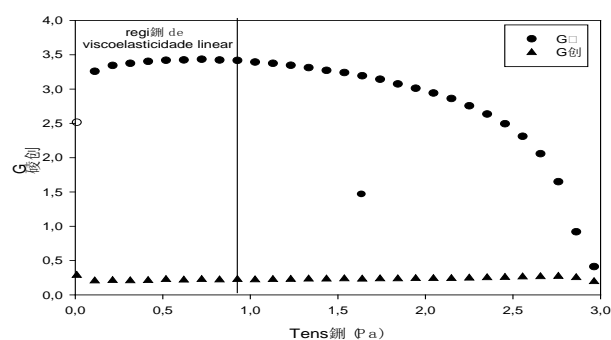


Fig. 2 G' and G'' curves in function of stress applied to system C1. Temperature: 25 °C

From these results, we performed a creep-recovery test, which provides information on the material's stability and determines the  $\eta_0$  (viscosity of the sample with shear approaching zero). This test is carried out by applying a constant stress to the material for a determined time interval, where this stress is chosen in the region of linear viscoelasticity. After this interval, the stress is removed (stress = zero) and the material's recovery from deformation is observed. The tests were carried out applying stresses of 0.1 and 0.3 Pa for thirty seconds, and material recovery times of ten and thirty minutes, respectively. The results presented in Figure 3 show that the values of  $\eta_0$  calculated for the stresses of 0.1 and 0.3 Pa were equal at 46,270 and 44,140 cP, respectively, which were mutually concordant. Besides this, we observed the recovery time from deformation of system C1, at different stresses. When a stress of 0.1 Pa was applied for thirty seconds, there was almost total recovery after about ten minutes, while under stress of 0.3 Pa for the same thirty seconds the recovery took about thirty minutes. These results evidence the recovery capacity of this fluid under the conditions tested.

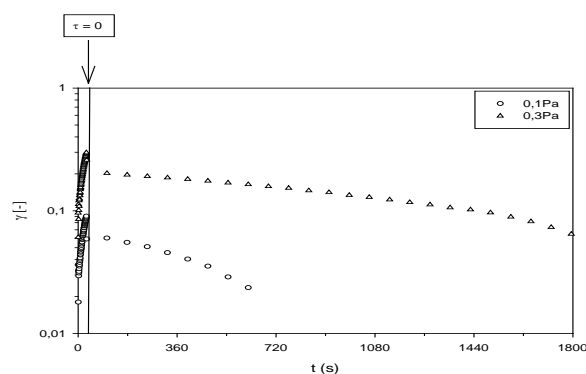


Fig. 3 Creep-recovery for system C1 at 25°C

## V. CONCLUSIONS

Among the surfactants tested, formulation C1 had the smallest CMC ( $4 \times 10^{-3}$  %v/v) and greatest capacity to reduce surface tension ( $56 \text{ mNm}^{-1}$ ), at a low concentration ( $10^{-4}$  %v/v). Formulations C2, S3 and S2 showed mutually similar values for both CMC ( $\sim 10^{-2}$  %v/v) and reduction of surface tension ( $\sim 68 \text{ mNm}^{-1}$ ), at low concentrations.

Formulation S1 also showed good resistance to variations of pH and temperature, but it had low viscosity values. The formulations sensitive to increased temperature were C2, S2, S5 and S6, which evaporated at temperatures of 70, 80, 50 and 50 °C, respectively. The formulations sensitive to variations of pH were C2, S2, S3, and S4, which showed phase separation at pH values below 5, above 11, above 6 and below 4, respectively.

The variation of pH did not significantly influence the physico-chemical properties of formulation C1. The CMC remained practically constant throughout the pH range tested and the surface tension reduction power was only impaired at low pH values ( $\approx 2$ ). This formulation also performed best regarding resistance to temperature and pH. This behavior can be related to the amphoteric structure of the base surfactant contained in this formulation. Besides this, it has high viscosity at small shear rates, with viscosity falling as the shear rate increases. Creep-recovery tests also demonstrated the recovery from deformation capacity of this formulation under the conditions analyzed probably associated with the physico-chemical properties of this formulation.

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